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13. ABSTRACT (Maximum 200 words)

(SOME HIGHLIGHTS OF OUR RECENT WORK - =Provided the reference theoretical results required in the identification of the transient N4 Molecule[5]. =Developed new coupled-cluster methods for obtaining accurate Raman intensities, which are crucial to the identification of many polynitrogen species [6]. =Showed that it is unlikely to be able to synthesize N4 with only one of two molecules excited. Both need to be excited into either triplet or quintet states and caused to collide [9]. =Demonstrated that an ionic lattice composed of N5+ and N3- is not likely to exist [8]. =Proposed that the next target for the DARPA program should be to synthesize the pentazole anion, N5-, the 'inorganic benzene' [4,6]. =Predicted the properties of the pentazole anion using our high level couple-cluster methods, including its energetics, structure, vibrational frequencies, and IR and Raman intensities, and its UV-vis (electronic excited state) spectrum [6]. =Suggested that N5+ and N5- are likely to be able to co-exist in an ionic lattice, further recommending the synthesis of the anion [10]. =Performed a large number of high level quantum chemical calculations to survey all stable purely nitrogen species, from N2 to N10 and some larger species, their cations and anions. We provide the vibrational frequencies, IR and Raman intensities for all, and for selected molecules, excited and ionized state information. This information is collected into a Compendium that can be downloaded from my web page [11]. =Recommended that we seriously consider synthesis of the N6O3 molecule, which by virtue of its three coordinate covalent bonds to oxygen, permits the long sought N6 pseudo-benzene ring to form. We report detailed studies of its activation barrier and properties in a recent paper [12].

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IDENTIFICATION AND SYNTHESIS OF HIGH NITROGEN PROPELLANTS

University of Florida

**Principal Investigator
Rodney J. Bartlett
Quantum Theory Project
University of Florida
2301 New Physics Building # 92
PO Box 118435
Gainesville, FL 32611-8435
Phone: 352-392-1597
FAX: 352-392-8722
Email: bartlett@qtp.ufl.edu**

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POLYNITROGEN FUELS: THE CONTRIBUTION OF PREDICTIVE THEORY

Rodney J. Bartlett
Quantum Theory Project
Departments of Chemistry and Physics
University of Florida, Gainesville, FL 32611-8435

INTRODUCTION

In 1989 we submitted a proposal to the AFOSR on the basic research topic of investigating 'metastability' in molecules, meaning states whose energies are far above the norm even for highly endothermic molecules. A consequence of such an investigation, might be ways to enhance the energy content of potential rocket fuels. The avowed objective of the initial HEDM program was to explore ways to make potentially revolutionary improvements in thrust to provide significant gains in payload. Metastability is one way to improve energy content. Metastability can occur due to long-lived excited states of a molecule, but no solution to trapping such states is apparent. The other alternative is what we termed 'geometric metastability' which means to put atoms together into a molecule in unusual ways, and depend upon the bonds formed to store the energy. An additional condition was that the perspective fuels had to be lightweight yet have more energy per mass unit than known bi-propellant species like LOX + H₂; or a molecule like hydrazine, as a mono-propellant. Since the molecules to be proposed are not known experimentally, and since synthesis and characterization of candidate systems would be very expensive and difficult; *only predictive quantum chemical methods make it possible to assess the energy content and kinetic stability (barrier to dissociation) of such structures, to identify the best prospects for success prior to any synthetic effort.* Modern quantum chemistry also provides very accurate spectroscopic signatures to identify such energetic molecules when they are formed, frequently even in very small quantities.

In our proposal we focused on low-mass molecules which had the capacity to store very large amounts of energy per mass unit. The prototype for such molecules would be polynitrogen systems, and in particular, purely nitrogen molecules. Replacing CH groups in an organic molecule by nitrogen atoms can significantly increase its endothermicity since the standard state for N is N₂, one of the stronger bonds known. This may also be viewed less quantitatively as increasing the N-N repulsions, since unlike CH-, N- carries a lone pair of electrons with it. As the perfect all nitrogen molecule would also 'burn' to just N₂ there would even be the bonus that it would be innocuous to the atmosphere and would leave no signature. Hence, in our proposal we suggested fascinating, speculative molecules like N₄ with the four atoms in a tetrahedral configuration[1,2], N₈ or the nitrogen analog of cubane[1,2], various pentazole species like NaN₅, N₅-N₅[3], and a wealth of others involving high nitrogen content together with heteroatoms[4]. None were known experimentally, but according to high level, predictive quantum chemical calculations, all could be shown to store large amounts of energy and to have significant barriers to dissociation, suggesting their probable formation under appropriate (not easily obtained) conditions. Our first report showing these results is in the Proceedings of the High Energy Density Materials Conference, in Feb, 1990, [1]. We reported the I_{sp} of N₄

would exceed LOX + H₂ and that it has a barrier to dissociation exceeding that of TNT. N₈ would also be very effective, though its computed barrier is about half that of N₄ [2]. We made similar studies of pentazole derivatives [3], and others [4].

Our suggestions were pursued in the AFOSR HEDM program, and then in this DARPA program, as well as by NASA, the latter two with the avowed intent to synthesize some of these pure nitrogen species. The following summarizes some of our recent accomplishments.

SOME HIGHLIGHTS OF OUR RECENT WORK

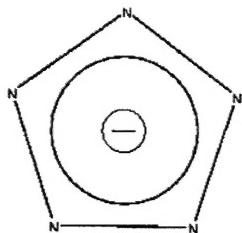
- Provided the reference theoretical results required in the identification of the transient N₄ Molecule [5]
- Developed new coupled-cluster methods for obtaining accurate Raman intensities, which are crucial to the identification of many polynitrogen species [6].
- Showed that it is unlikely to be able to synthesize N₄ with only one of two molecules excited. Both need to be excited into either triplet or quintet states and caused to collide [9].
- Demonstrated that an ionic lattice composed of N₅⁺ and N₃⁻ is not likely to exist [8].
- Proposed that the next target for the DARPA program should be to synthesize the pentazole anion, N₅⁻, the 'inorganic benzene' [4,6].
- Predicted the properties of the pentazole anion using our high level couple-cluster methods, including its energetics, structure, vibrational frequencies, and IR and Raman intensities, and its UV-vis (electronic excited state) spectrum [6].
- Suggested that N₅⁺ and N₅⁻ are likely to be able to co-exist in an ionic lattice, further recommending the synthesis of the anion [10].
- Performed a large number of high level quantum chemical calculations to survey all stable purely nitrogen species, from N₂ to N₁₀ and some larger species, their cations and anions. We provide the vibrational frequencies, IR and Raman intensities for all, and for selected molecules, excited and ionized state information. This information is collected into a Compendium that can be downloaded from my web page [11].
- Recommended that we seriously consider synthesis of the N₆O₃ molecule, which by virtue of its three coordinate covalent bonds to oxygen, permits the long sought N₆ pseudo-benzene ring to form. We report detailed studies of its activation barrier and properties in a recent paper [12].

DISCUSSION

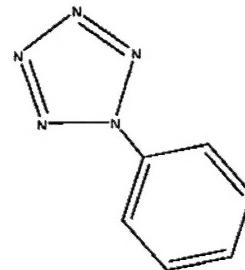
In the DARPA program there has been a potential observation of N₄ [5], using our predictions of the vibrational spectra and IR and Raman intensities for identification [6]. Also substantial success has been achieved with the synthesis of N₅⁺AsF₆⁻, however, that molecule is still a long way from a pure nitrogen species or even a fuel, until we can replace the As F₆⁻ [7] group with a light, suitable anion. If it were also composed of only nitrogen, we would meet our objective. Through this work we now have the N₅⁺ unit as a potential partner in forming purely nitrogen species.

Our main objective this past year was to consider the prospects for combining N_5^+ with the well-known azide anion, N_3^- [4,8]. However our studies demonstrated that it was unlikely to be possible to combine the two, primarily because the extreme electron affinity of N_5^+ demands an anion with a similar ionization potential to maintain the integrity of the ion-pair, and that is not the case for N_3^- . There are other factors like lattice stabilization energies that contribute to stabilizing ionic crystals, but once there can be significant electron transfer, then much lower energy covalent bond formation is likely. We found several covalent forms of N_8 , which would seem to be favored over the $[N_5^+][N_3^-]$ [4,8] pair.

On the other hand, our proposed pentazole anion, N_5^- [3,6]



seems to be better suited to making such a crystalline pair. The latter molecule is the ‘inorganic benzene’, as it is delocalized and assumes an exact pentazole shape with all bond lengths being equal. It is amazing that this inorganic pentazole is not known experimentally[3]. That is, it has never been synthesized in a salt like AgN_5 , or $Mg(N_5)_2$, or Some other similar species[4]. The pentazole ring, as opposed to the anion,



is known experimentally as a phenylpentazole e.g., where the large phenyl group and other similar organic groups form a covalent bond to N and stabilize the pentazole ring. In the salts above, we would anticipate an inorganic structure where the N_5^- unit maintains its anion character and could potentially be used as a component in synthesizing other structures. In particular, we might hope to be able to combine N_5^+ with N_5^- .

Among the different concepts that have been introduced in designing energetic materials, this suggests investigating very high energy ionic lattice structures composed of species where the corresponding neutrals, themselves, are not likely to be stable. In this sense, there is an analogy to excimer laser design, where since the excited states are bound, while the ground states are not, population inversion can be achieved. For N_5^+ and N_5^- , the ionized state is greatly preferred over either of the radicals, which would be likely to immediately fall apart.

We have made an initial investigation of the possible crystal structures that can occur for the $[N_5^+][N_5^-]$ ion pair[10]. We are continuing to explore the solid-state form and the degree of stability achieved due to the lattice.

As a by-product of this work, we have encouraged several experimental physical chemistry research groups (Neumark, Lineberger, Compton) to look for the pentazole anion via electron detachment or some other procedure which will establish its existence; while also suggesting it as a target of synthetic groups.

Whereas it is quite difficult to synthesize purely nitrogen species, since in many cases the chemistry does not yet exist; having at least one C atom can change the story dramatically. For example, replacing one N- by CH- gives the cyclic tetrazole anion, which is comparatively well known[15]. Though less well known, making a similar replacement in the N_5^+ cation, provides three possible $(CH)N_4^+$ cations that have much in common with N_5^+ . However, unlike purely nitrogen species, these molecules can use known elements of CN heterocyclic chemistry for their synthesis[15]. Hence, they can offer a potential stand-in for the $[N_5^+][N_5^-]$ system. Furthermore, several different species can be made by replacement of 1-5 N by CH. This is exactly the kind of study that lends itself to a prior theory investigation, as many of these candidate systems can be investigated in terms of their electron affinities, ionization potentials, crystalline structures, and reaction paths. We have recently made such computations.

In quite interesting work recently reported by Hemley, et al. [16], the prospect of forcing liquid nitrogen under pressure to undergo a phase transition into another form obviously stores energy, since any such species must have a higher heat of formation. Hence, the solid state form of N is of great interest. If the process of formation can be made efficient, if it can be formed in quantity, and if it is sufficiently stable once formed, this could be an ideal fuel. At this point, the actual form of the material is unknown. We have explored new quantum chemical methods with periodic boundary conditions to further aid in the identification of the species and its energy content.

There may well be units in the solid that have characteristics in common with the exotic N molecular forms we have studied. The theoretical investigation of three dimensional N solid state forms is not as predictive as is the theory for isolated molecules, but some progress can be made[14]. In our case, we used the CRYSTAL program to perform some Hartree-Fock and DFT calculations plus new wavefunction methods like MBPT(2) we have developed[17]. The polymeric form of N has been studied with the following results:

The continuing experimental search for N_4 and now for N_5^- recommends that we have a means to detect very small quantities. Vibrational spectra is not the best tool for detection, though that is the only one used to date. Instead, it would be quite nice to be able to use laser induced fluorescence (LIF). However, unlike vibrational spectra, the theory demands for LIF are far more severe. At the very least we need a survey of the structures of bound excited states, and then some Franck-Condon analysis to suggest where the emission band will occur. Our EOM-CC and STEOM-CC tools are the state-

of-the-art in excited state studies, and we also have analytical gradient tools to locate extremum points on excited state surfaces, but this is still a highly demanding task. We propose to explore the excited states and add a FC analysis to assist in this endeavor.

COMPUTER EXPERIMENT

Instead of budgeting all our computer money for local computer access, as has been done previously, we thought this project could benefit more from purchasing a four processor, high performance PC configuration. We did so and have made extensive benchmarks for executing ACES II on such PC's using both Linux and NT (these are available on request). The timings recommend this configurations for many of our routine HEDM applications.

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